Abstract

Multi-scale modeling of two-dimensional layered nanomaterials built of carbon, boron, and nitrogen atoms

Two-dimensional materials and their alloys remain under interest of scientists, due to their very appealing and conceivably tunable properties. $C_xB_yN_{1-x-y}$ graphene-like alloys constitute intriguing class of materials, including B- and/or N- doped graphene, C-doped hexagonal boron nitride (hBN), mixtures of graphene and hBN, or CBN structures with long-range order. Many reports on synthesis of such alloys are available, as well as numerous theoretical predictions for varied configurations of constituent C, B, N atoms. However, the deep understanding of the equilibrium morphology, stability, and phase diagrams of these interesting two-dimensional compounds is still lacking.

We address these issues in the present thesis. In the first step, we investigate the stability of the 2D ternary disordered C-B-N systems for the wide range of possible compositions, employing: (i) DFT-based Cluster Expansion technique, and (ii) direct valence force field approach for systems with thousands of atoms. We find the most energetically favourable configurations of C-B-N alloys via combination of (i) and (ii) with Monte Carlo Metropolis simulations. This allows us to avoid artificial periodicity, often introduced in *ab initio* simulations (when using small supercells). We find out that all investigated systems deviate strongly from random alloys and exhibit short-range ordering, *i.e.,* avoid creating N-N and B-B bonds in graphene lattice and have tendency to form graphene and hBN domains in ternary alloys.

We attempt to establish (in an iterative scheme) the effective Heisenberg-like hamiltonian parameters in Cluster Expansion models for graphene doped with N/B, and evaluate their quality. In order to use empirical potentials reasonably, we perform extensive tests of available VFFs including Tersoff, ReaxFF and COMB3 to find that none of them is fully satisfactory for simulations of CBN alloys. We combine and modify existing Tersoff parametrizations improving its performance.

Lastly, we show exemplary results for graphene flakes, and comment on Density of States of a chosen structures determined in Empirical Tight Binding approach.